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Structural and electrical properties of $SrBi_2V_xNb_{2-x}O_9$ ferroelectric ceramics: Effect of temperature and frequency

Sameer Jain · A. K. Jha

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Abstract Aurivillius type bismuth layered materials have received a lot of attention because of their application in ferroelectric non-volatile random access memories. Among bismuth layer structured ferroelectric ceramics $SrBi_2Ta_2O_9$ (SBT)/$SrBi_2Nb_2O_9$ (SBN) are of great interest for researchers because of their fatigue resistance and less distorted structure. Recently vanadium substitution in SBN/SBT has shown interesting electric and dielectric properties. In the present work, processing conditions, microstructure and electrical studies of vanadium doped SBN ferroelectric ceramics have been performed. Samples of compositions $SrBi_2V_xNb_{2-x}O_9$, x=0.0, 0.1, 0.3, 0.5 were prepared by solid-state reaction technique using high purity oxides / carbonates. The samples were calcined at 700 °C and sintered at 800 °C. X-ray diffractograms show that a single phase layered perovskite structure is formed in all the samples. Effect of partial substitution of pentavalent niobium ion (0.68 Å) by smaller pentavalent vanadium ion (0.59 Å) at B site on the microstructure, Curie temperature, Dielectric constant, Dielectric loss and electrical conductivity have been investigated. Dielectric properties of SBVN have been investigated from room temperature to 500 °C and frequency of 100 Hz to 1 MHz. Dielectric constant values at their respective Curie points are observed to increase with increasing vanadium concentration. Curie temperature is observed to be maximum in x=0.1 vanadium doped sample. Strong relaxor like dielectric relaxation at the transition temperatures have been observed. With increasing vanadium concentration the dielectric loss is observed to increase significantly. It is also observed that dielectric loss increases with increase in temperature. The variation of conductivities in these samples is also reported.

Keywords Ferroelectrics · Curie temperature · Dielectric constant · Dielectric loss

1 Introduction

$SrBi_2Nb_2O_9$ (SBN) and $SrBi_2Ta_2O_9$ (SBT) have attracted attention of researchers in recent years as potential materials to replace lead zirconate titanate (PZT) for ferroelectric random access memories (FeRAMs) applications [1–5]. Large remanent polarization, low coercive field, low leakage current, high Curie temperature, lower sintering temperature and being lead free are some of the important characteristics which make $SrBi_2Nb_2O_9$ an alternative to PZT for FeRAM applications [6–8]. Bismuth layered Aurivillius type compounds have a general formula

$[Bi_2O_2]^{2+}$ $[A_{n-1}$ B_n $O_{3n+1}]^{2-}$ (n=1,2,3,4) consisting of perovskite $[A_{n-1}$ B_n $O_{3n+1}]^{2-}$ structure sandwiched between paraelectric $[Bi_2O_2]^{2+}$ layers. Here, A can be a divalent element like Ba^{2+}, Sr^{2+}, Pb^{2+},Ca^{2+} etc. and B can be Nb^{5+}, Ta^{5+}, Mo^{5+}, W^{6+}, Fe^{3+}, Ti^{4+}, V^{5+} etc. The role of bismuth oxide layer in influencing the electrical and ferroelectric properties of these ceramics has been found to be critical [9]. These ceramics are very sensitive to compositional variations. Doping at different sites modify the structure and influences properties of these materials. There are reports on the structural and dielectric properties of low concentration (up to 15 at.%) vanadium substituted SBN sintered at lower temperature [10–13]. However, the usual sintering temperature in SBN is about 1200 °C. It is, therefore, a matter of interest to prepare and study

S. Jain · A. K. Jha (✉)
Thin Film and Materials Science Laboratory,
Department of Applied Physics, Delhi College of Engineering,
Delhi 110042, India
e-mail: dr_jha_ak@yahoo.co.in

vanadium doped and undoped SBN under identical conditions at different sintering temperatures. In the present work, undoped and vanadium doped SBN have been prepared at different sintering temperatures and their structural, dielectric, electrical and ferroelectric characteristics have been investigated.

2 Experimental

Samples of compositions $SrBi_2Nb_{2-x}V_xO_9$ (SBNV); x=0.0, 0.1, 0.3, 0.5 (SBN, $SBNV_{0.1}$, $SBNV_{0.3}$, $SBNV_{0.5}$) were prepared using solid-state reaction method. The starting powders $SrCO_3$, Bi_2O_3, Nb_2O_3, V_2O_5 (all from Aldrich of 99.9% purity) were taken in stoichiometric proportions and ground and then calcined in air for 2 h at 700 °C. The calcined powders were ground and mixed with about 1.5 wt.% polyvinyl alcohol (Aldrich) as a binder and pressed to form pellets by applying uniaxial pressure of ~300 MPa. These pellets were sintered at 800 °C for 2 h in air. X-ray diffractograms were recorded using CuKα radiations (range $10°\leq 2\theta \leq 70°$). For dielectric property measurement, the sintered pellets were polished to a thickness of ~1 mm and silver pasted on both sides and cured at 550 °C for 30 min. The dielectric measurements were carried out from room temperature to 500 °C using Agilent 4284A LCR meter at oscillations amplitude of 1 V.

3 Results and discussions

Figure 1 shows the X-ray diffractograms of the sintered samples. Lattice parameters have been calculated from the obtained d-values. The values of calculated lattice parameters are listed in Table 1. X-ray analysis reveals that all the samples have an orthorhombic perovskite structure. This implies that the layered perovskite structure of $SrBi_2Nb_2O_9$ is preserved in $SrBi_2Nb_{2-x}V_xO_9$. However, a small variation in the position and intensity of the peaks is observed indicating a variation in the lattice parameters. Increased background noise in the doped sample indicates decreased crystallinity of the structure. It is observed that there is a small decrease in peak width in the doped samples. The peak positions in the doped samples shifts towards the

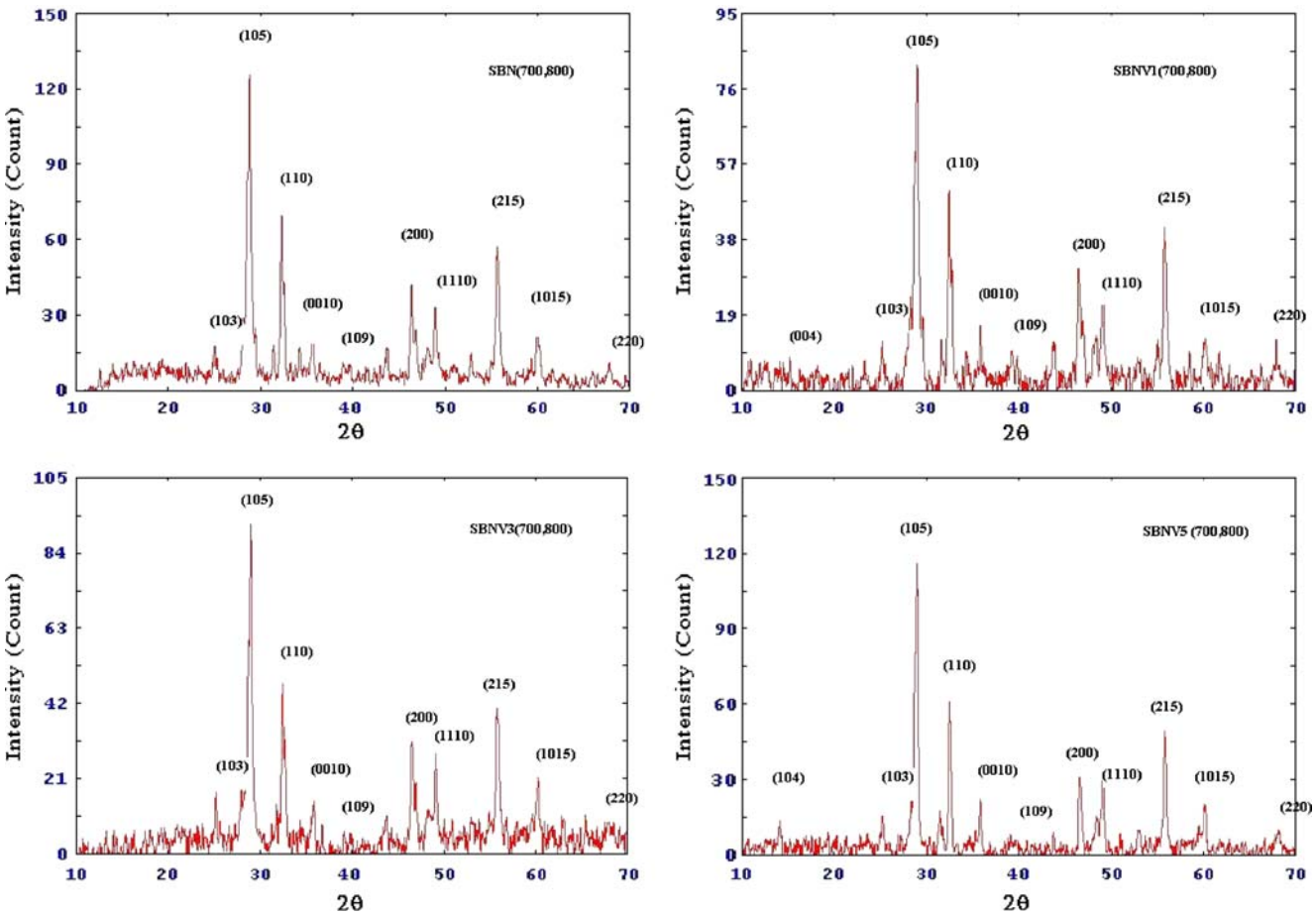

Fig. 1 X-ray diffractograms

Table 1 Ionic radii, coordination numbers and lattice parameter.

Ions	IR (Å)	CN	*x*-Values	a (Å)	b (Å)	C (Å)	Unit cell volume (Å)^3
Sr^{2+}	1.44	12	0.0	3.9155	3.9280	25.3184	389.4050
Bi^{3+}	0.96	5	0.1	3.9052	3.8984	25.000	380.6007
Nb^{5+}	0.68	6	0.3	3.9052	3.8939	25.0344	380.6845
V^{5+}	0.59	6	0.5	3.9012	3.8960	25.1100	381.6480

right, e.g., the peak (105) is at 2θ=28.835 °C for pure SBN which shifts to 2θ=29.025 °C for the samples with x=0.1.

The change in lattice parameters is expected on substituting smaller vanadium ion (ionic radius 0.59 Å) for niobium ion (ionic radius 0.68 Å). It is observed that doped samples show an overall very small decrease in parameter 'a' in comparison to pure SBN. Such type of change in lattice parameter in 'a' may be due to the structural constraint induced by the $[Bi_2O_2]^{2+}$ interlayer [14]. This $[Bi_2O_2]^{2+}$ layer does not allow the crystal lattice to shrink at low doping concentrations. At higher doping concentrations the shrinking tendency of the crystal lattice overcome the $[Bi_2O_2]^{2+}$ constraint. It is also noted that lattice constant 'c' shows a slight increase with increasing vanadium concentration. The unit cell volume of the doped samples show an overall decrease in comparison to pure SBN. Among doped samples there is no appreciable change in unit cell volume with increasing vanadium concentration. This indicates an increased rattling space available for the cations at B-site [10]. Tetragonal strain (c/a) of the samples was calculated from the obtained lattice parameters. Tetragonal strain of SBNV samples shows a small increase as compared to that of undoped $SrBi_2Nb_2O_9$. Lattice distortions have significant influence on the dielectric properties of bismuth layered ferroelectric materials [9, 15].

Figure 2 shows the variation of dielectric constant as a function of temperature at 100 kHz. The temperature at which phase transition occurs corresponds to the Curie temperature of the sample. Curie temperature is observed to increase from 400 °C for $SrBi_2Nb_2O_9$ to 410 °C for $SrBi_2Nb_{1.9}V_{0.1}O_9$ sample while it is observed to decrease slightly in the samples with higher concentration of vanadium. The increase in Curie temperature in $SrBi_2Nb_{1.9}V_{0.1}O_9$ is possibly due to the smaller size of vanadium ion which results in larger rattling space. Wu et al have also reported similar results [13]. Curie temperature is observed to decrease slightly in the samples with x=0.3 vanadium content. The Curie temperature of the ferroelectrics depends upon the polarizability of the material. Electronic polarization of vanadium doped SBN possibly reduces due to smaller size of the vanadium. This is also the cause of lower Curie temperature in the samples with higher vanadium content. These results are in contradiction with earlier reports [13]. However the sintering temperature used in there work is different, further experimentation under identical sintering conditions is required.

As also seen in Fig. 2 a sharp transition is observed in both doped and undoped samples. An increase in dielectric constant with vanadium content is observed. The dielectric constant of a material has four polarization contributions:

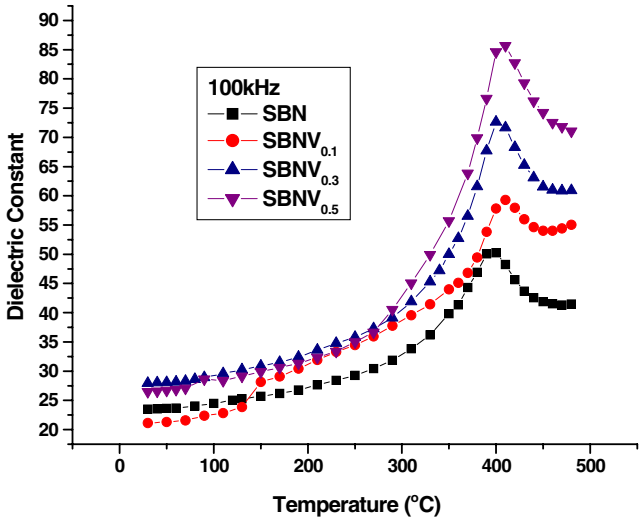

Fig. 2 Variation of dielectric constant with temperature at 100 kHz

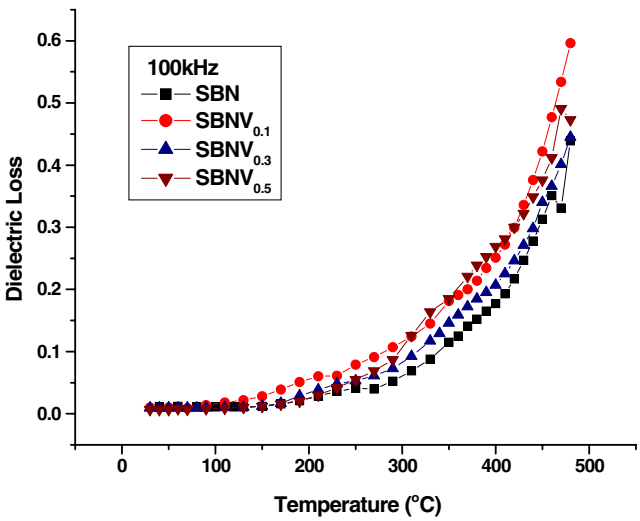

Fig. 3 Variation of dielectric loss with temperature at 100 kHz

(1) electronic polarization (2) ionic polarization, (3) dipolar polarization and (4) space charge polarization. At low electric field contribution from dipolar polarization cannot be significant. Only ionic and electronic polarizations contribute significantly to dielectric constant at low electric fields and 100 kHz oscillation level. Due to smaller ionic radius of vanadium the electronic polarization is expected to reduce. Also ionic polarization depends on lattice constants and unit cell volume [13]. The variation in transition temperature is explained both in terms of changes in covalancy of interatomic bonding and volume of the unit cell, although both are interrelated. Here the changes have been correlated directly to explain the variation in transition by the observed changes in unit cell volume [13]. A decrease in lattice constants in vanadium substituted samples is expected due to smaller ionic radius of vanadium than that of niobium. It is observed (Table 1) that there is negligible change in lattice constants and unit cell volume of the doped samples. This may be due to the structural constraint imposed by $[Bi_2O_2]^{2+}$ interlayer which prevents the shrinkage of crystal lattice [14]. This results in an increased ionic polarization with increasing vanadium content. An increase in dielectric constant with vanadium content indicates that the increase in ionic polarization is predominant over the decrease in electronic polarization. It is known that the increase in transition temperature corresponds to an increased polarizability which can be understood by enlarged rattling space available in vanadium substituted samples. This would make the domain motion easier and increase the dielectric permittivity which in turn explains the increase in dielectric constant.

Figure 3 shows the variation of dielectric loss with temperature at 100 kHz. The dielectric loss of SBN at Curie temperature is 0.177 and that of $SBNV_{0.1}$ at Curie temperature is 0.299. There is an overall increase in the loss in the vanadium doped samples. The loss values show

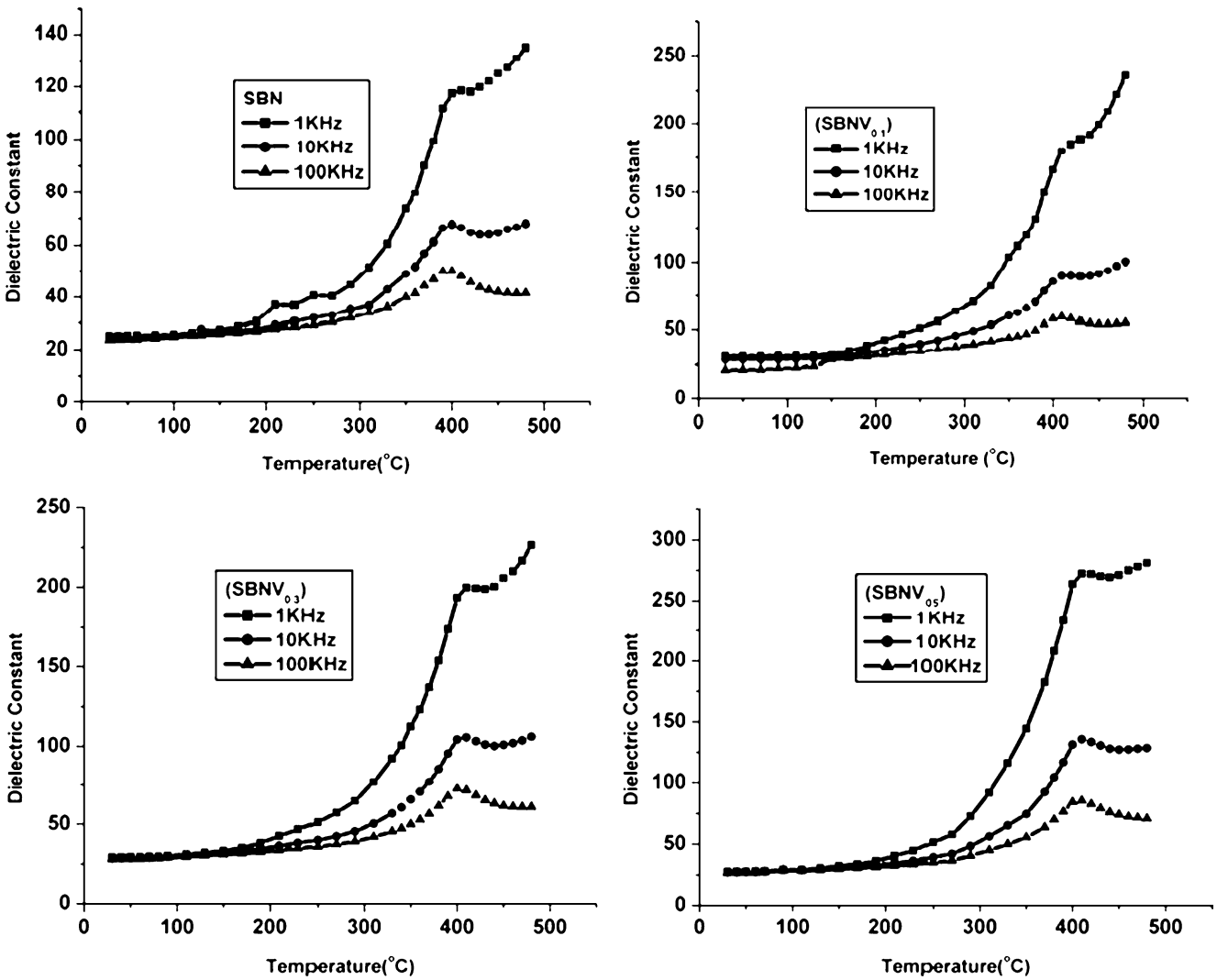

Fig. 4 Variation of dielectric constant with temperature at different frequencies

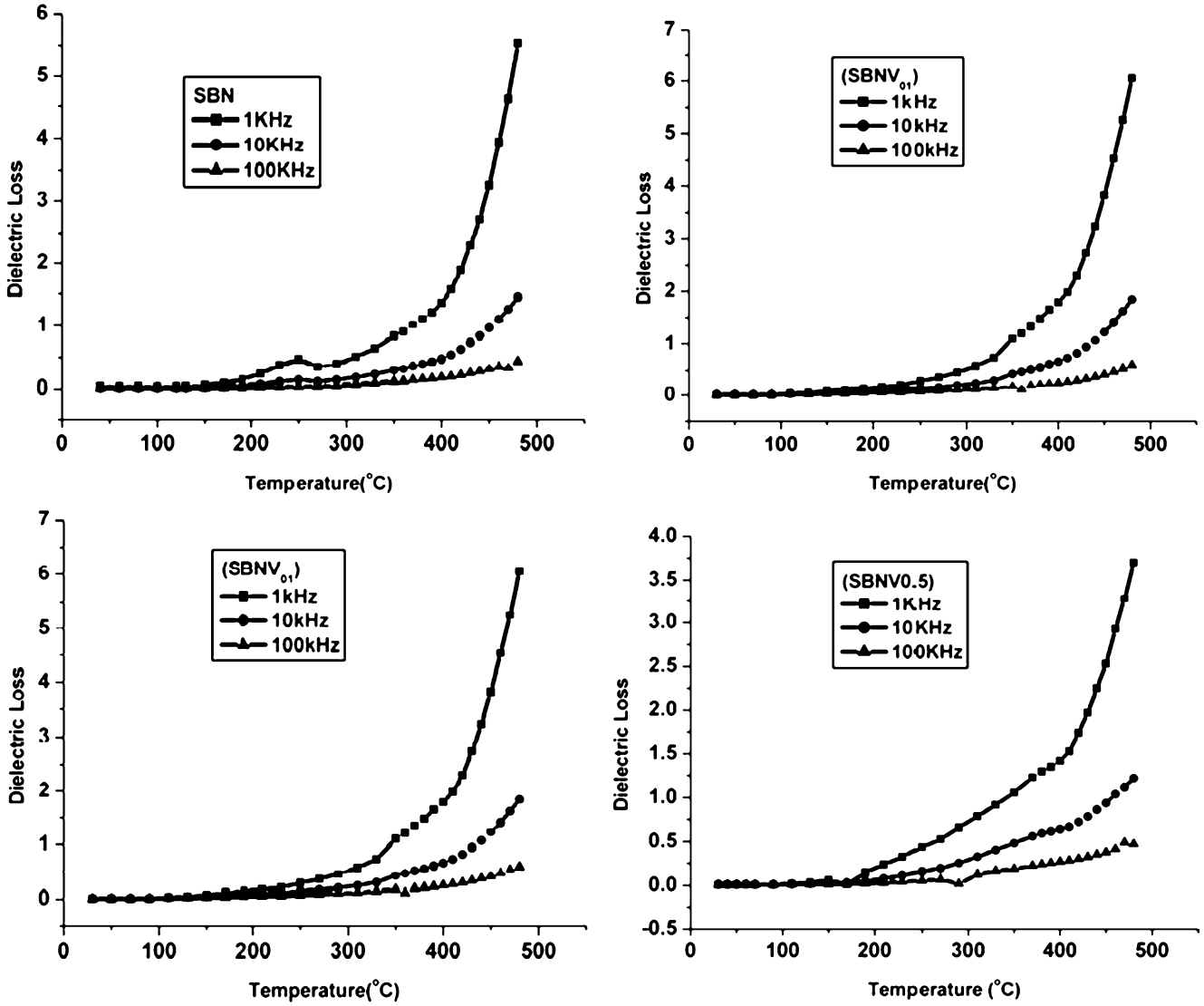

Fig. 5 Variation of dielectric loss with temperature at different frequencies

negligible change up to 250 °C temperature. Dielectric loss increases with increase in temperature and the increase is sharp at higher temperature. Dielectric loss is observed to be least in the pure SBN and highest in $SBNV_{0.1}$ sample at their respective Curie points. The behavior of loss values can be explained using intrinsic defect formation at higher temperature. The formation of defects in the structure because of bismuth evaporation at high temperature is expected. Therefore, the samples should possess vacancies due to evaporation of bismuth and oxygen generating charge carriers [16]. The introduction of vanadium in place of niobium would make it easier to release the charge carriers at higher temperature and therefore doped sample would show higher loss in comparison to the undoped sample at higher temperatures.

Figure 4 shows the dielectric constant measured at 1, 10, and 100 kHz as a function of temperature. The observations

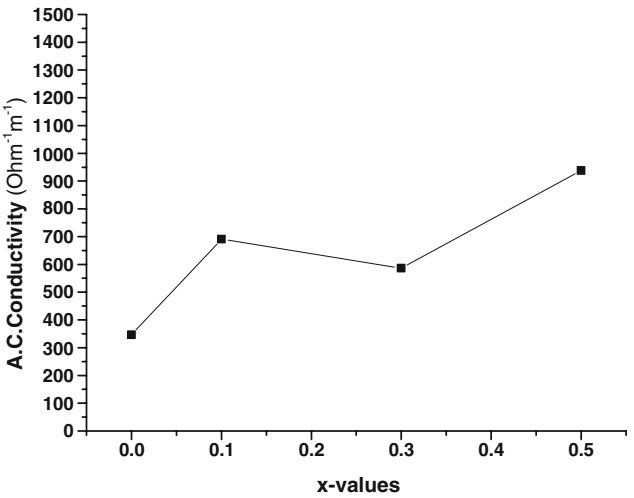

Fig. 6 Variation of a.c. conductivity with *x*-values

are similar to those reported in other systems [17–19]. The peak of curves i.e. the maximum permittivity is observed to decrease with increasing frequency in all the samples. As the frequency increases the maximum value of permittivity decreases and the overall nature approaches the normal relaxors behavior. These features are typical of a thermally activated Debye relaxation in these frequency regions. The subsequent monotonous increase of dielectric constant at higher temperature is due to increase in conductivity [20–21]. The apparent transition temperature remains the same at all the frequencies. The broadness of curve possibly arises due to heterogeneity present in the material. Increased permittivity at the higher temperature may be due to the mobile charge carriers, which are due to the oxygen vacancies. The oxygen vacancies related polarization become more prominent at elevated temperature due to the increased space charges which acts as oxygen vacancies [11]. An increase in permittivity upon decreasing the frequency indicates a large contribution to dielectric constant due to space charge polarization in the doped samples.

Figure 5 shows the dielectric loss measured at 1, 10 and 100 kHz as a function of temperature. Dielectric loss decreases with increase in frequency. The loss in these materials is caused by space charge and domain wall relaxation [13]. Atomic, ionic and space charge polarizations are the main contributions to dielectric loss in these ceramics. The low electric field applied is too small to change the spontaneous polarization. Response frequencies for atomic and ionic polarizations are 10^{15} and 10^{13} Hz respectively. Space charge polarization has a response frequency of 100 Hz [14]. At higher frequencies space charge polarization does not exist and hence dielectric loss decreases with increasing frequency. The presence of oxygen vacancies which acts as space charges, contribute to the electronic polarization which can be related to dielectric losses. As discussed above, substitution of vanadium effectively enhances the concentration of oxygen vacancies in doped samples. This is consistent with the observed increase in dielectric loss in vanadium substituted SBN. It is reasonable to assume that the space charge is the main reason for an increase in dielectric loss.

Figure 6 shows the variation of a.c. conductivity with vanadium content. a.c Conductivity of all the studied samples has been calculated using the relation:

$$\sigma_{a.c.} = 2\pi f\, \varepsilon_o \varepsilon_r D$$

Where f is the frequency, ε_o is the permittivity of free space, ε_r is the dielectric constant and D is the dielectric loss. It is observed that conductivity values of all the vanadium doped ceramics are higher than that of the undoped sample.

4 Conclusions

It is concluded from the present work that vanadium substitution in SBN at B-site enhances dielectric constant. It is also observed that there is an overall increase in ferro-paraelectric transition temperature of vanadium doped samples as compared to pure SBN. Also vanadium doped SBN ceramics have been found to exhibit strong low frequency dielectric dispersion. Dielectric loss is observed to be higher in the vanadium doped SBN. Also, there is an overall increase in a.c. conductivity with vanadium substitution.

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